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MINERAL ACIDS WHICH CAUSE SOIL ACIDITY

By

Charles Danziger Samuels

A Thesis Submitted for the Degree of

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Mineral Acids Which Cause Soil Acidity.

Within recent years the subject of soil acidity has received much attention. This has resulted in the formulation of several theories regarding its cause and nature. One of the more important theories advanced to explain this condition in mineral soils is the mineral theory of soil acidity.

The mineral theory ascribes the acidity to the products formed from the weathering of minerals. In this weathering, the principal factor is the leaching of the silicates by carbonated water which dissolves the soluble bases and leaves the insoluble acid silicates. These acid silicates when present in sufficient amounts cause the soil solution to become acid which condition is unfavorable for the growth of many agricultural plants.

Historical.

The investigations of Way (1) are some of the earliest showing the replacement of bases in soils. The basic portion of ammonium , magnesium, sodium and potassium salts in solution were completely removed in their passage through columns of soil and equivalent amounts of calcium were found in the filtrates. The acid portion of the salt was unaffected in its passage through the soil. Way believed the action to be chemical and caused by a hydrated aluminum silicate occurring principally in the clay portion. He later artificially prepared several hydrated aluminum silicates which showed this property of basic exchange.

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A similar phenomena noted by Way of the replacement of bases occurs in acid minerals. This was first reported by Lemberg (2) who found that water could also act in the replacement of a base. In this case an acid silicate is formed.

Sullivan (3) discussed the mechanism of basic exchange and believed it to be a chemical phenomena. Upon filtering a solution of magnesium chloride through kaolin he found the filtrate to be acid. This acidity he described to the exchange of magnesium for iron and aluminum and their consequent hydrolysis. He based his conclusion upon the fact that the amounts of trivalent bases in solution "are of the same order of magnitude", as the acidity developed.

Cornu (4) after investigating the reaction of 150 minerals concluded that the formation of acid minerals involves an exchange between the hydrogen of the acid and the base of the mineral. He cited the reaction:

$H_4 Ca Al_2 Si_2 O_{10} + 2 CH_3 COOH = H_4 Al_2 Si_2 O_9 + Ca(CH_3 COO)_2 + H_2O$

He drew this conclusion from the fact that all the unweathered rock minerals are alkaline while those which have been leached for a considerable time are acid.

He states that many samples of kaolin are acid and that it is merely a matter of forming enough kaolin by weathering so that its acidic properties will predominate over the alkaline reaction of the original mineral and thus cause an acid reaction of the resulting silicate.

Clarke (5) has investigated the reaction of extracts of several soil forming minerals and found they were either alkaline or neutral.

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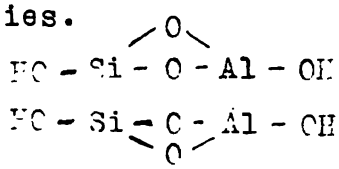
Steiger (6) determined the Na_2O equivalent of the evaporated extracts which Clarke had tested. He found no relation at all between the amount of salt present and the reaction to indicators.

Daikuhara (7) leached minerals with carbonated water and in every case the mineral became more acid. The extract from the minerals contained considerable MgO, CaO, Na_2O, Fe_2O_3 and small amounts of P_2O_5, SiO_2 and K_2O. He also stated that the soil from acidic rocks will develop more acidity than that from basic rocks.

The workers mentioned and others who have noted the reaction of primary minerals agree that they are alkaline in reaction. Cornu and Daikuhara have shown that upon the removal of bases from silicates they become acid. This removal of bases changes of course the chemical composition and chemical properties of the mineral. The various materials which might be formed upon the weathering of primary minerals are thoroughly discussed by Van Hise (8). Along with the change in chemical composition and properties there may also be a change in structure. The structural diagrams of the various silicates are discussed by Clarke (9). This work will be mentioned more in detail in connection with the discussion of experimental results.

Loew (10) has developed a structural formula for kaolin which is of interest in connection with acid soils. He considers the OH groups (a) and (b) important in giving the molecule both acidic and basic properties.



(a) (b)

The structure being a balanced one represents the stability

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of the kaolin molecule.

Conner (11) in studying the acidity of zeolites comments upon the effect of constitution upon acidity. In the summary he says: "The acidity of aluminum silicate is not only in proportion to the ratio of Al_2O_3 to $Si\ O_2$ but also in proportion to the water of constitution. The greater the proportion of water in the silicate the more acid is the reaction." A consideration of the mineral composition of the soil is important, for the acidic properties of the soil depend largely upon the nature of the original minerals from which the soil is derived. Robinson in a petrographic study of thirteen widely distributed soils and subsoils of the United States found feldspar and muscovite in large amounts in most of the soils. The minerals epidote, biotite, tourmaline, magnetite, hornblende, apatite and zircon were present in appreciable quantities in many of the soils.

The first investigators of the acidity of both mineral and highly organic soils ascribed the condition largely to organic acids. Within recent years, however, the mineral portion of the soil has been considered to be of much greater importance in this connection, especially in the case of mineral soils. There is little information, however, upon the nature of the various mineral acids. The writer has not found any work which deals with the amount of acidity that may be developed by different minerals upon weathering and the hydrogen ion concentration of water suspensions of the acids formed. It was thought that the reason some soils develop a very much higher acidity than others is due to the larger amounts of some particular mineral or minerals that

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they originally contained and which have weathered into very strongly acid residues. The purpose of the present investigation was to determine if this might be the case.

Experimental

Formation of acid residues by leaching.

In the following leaching experiments ten minerals were used, viz; kaolin, muscovite, olivine, diopside, tremolite, orthoclase, biotite, apophyllite, natrolite and chrysocolla.

These minerals were ground to pass a 100 mesh sieve. Two hundred gram samples of each of the ground minerals were then placed in two liter bottles and one liter of carbonated water added to each. The bottles were shaken intermittently by hand to aid solution and filtered at the end of forty eight hours. The solutions were evaporated almost to dryness in 600 cc. beakers, the residues transferred to weighed evaporating dishes, dried at 110° and weighed. The minerals were returned to the bottles and the treatment repeated twenty one times.

The acidity or alkalinity of the minerals was determined after each extraction. This was done by placing a piece of litmus paper in contact with the mineral for one half hour.

The relation between the reaction of the minerals and the amount of base extracted at each leaching is of interest. Orthoclase, muscovite, biotite and chrysocolla showed an abrupt decline in the amount of material extracted when the originally alkaline minerals become acid in reaction. As suggested by Cornu with the removal of sufficient basic material the hydrated aluminum silicates predominate in the residue which is accordingly acid. This apparently is the case with the minerals mentioned.

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Table 1.

The weight in grams of material extracted from 200 gram samples of minerals by successive one liter portions of carbonated water. Extracts were made every two days.

Time in days	Kaolin	Muscovite	Olivine	Diopside	Tremolite
2	.0412*	.7476	.7265	2.0739	1.0480
4	.0094	.2103	.2455	.2346	.8267
6	.0111	.1649	.0830	.2072	.7874
8	.0145	.1947	.0821	.1730	.8997
10	.0148	.0812*	.0796	.0638	.7487
12	.0160	.0794	.0760	.1324	.7550
14	.0077	.0656	.0576	.1234	.7402
16	.0113	.0640	.0531	.1124*	.7808
18	.0050	.0508	.0694	.1038	.7572
20	.0061	.0432	.0578	.0760	.6760
22	.0083	.0470	.0621	.0794	.6120
24	.0062	.0430	.0610	.0696	.5845
26	.0048	.0320	.0622	.0746	.6005
28	.0054	.0340	.0581	.0788	.6144
30	.0061	.0340	.0562	.0804	.6026
32	.0050	.0320	.0386	.0810	.5294
34	.0047	.0270	.0322	.0764	.4498
36	.0039	.0450	.0464	.0814	.4764
38	.0042	.0278	.0461	.0703	.4958
40	.0033	.0241	.0456	.0711	.4278
42	.0037	.0219	.0470	.0694	.4300
Total	.1927	2.0695	2.0861	4.1329	13.8429
% Leached	.19%	2.07%	1.04%	2.07%	6.92%

Time in days	Orthoclase	Biotite	Apophyllite	Natrolite	Chrysocolla
2	.4150	.3846	.4679	.2447	.6098
4	.3886	.1022	.4936	.1452	.4884
6	.0816	.1128	.2325	.1200	.3742
8	.0490	.0660	.2477	.0980	.4342
10	.0438	.0558	.1132	.0760	.2904
12	.3908	.0802	.1840	.0584	.2924
14	.3948	.0320	.1244	.1280	.2400
16	.3074	.0377	.1459	.0815*	.3034
18	.3296	.0373	.0737	.0675	.0656
20	.2294	.0080	.1520	.0454	.1710*
22	.3046	.0076*	.1035	.0586	.1528
24	.2184	.0081	.1235	.0432	.1788
26	.1424	.0062	.1080	.0411	.1242
28	.0350*	.0031	.1630	.0398	.1288
30	.0298	.0047	.1120	.0376	.1274
32	.0242	.0052	.1011	.0349	.1169
34	.0316	.0034	.0890	.0351	.1012
36	.0314	.0031	.0761	.0311	.1138
38	.0146	.0033	.0421*	.0290	.1162
40	.0166	.0028	.0319	.0317	.1089
42	.0140	.0040	.0321	.0300	.1074
Total	3.4926	1.0614	3.2187	1.6547	4.7444
%Leached	1.75%	1.06%	1.61%	.83%	2.37%

* Point in weathering at which litmus paper indicated definite acidity of residue.

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This explanation cannot be applied to the diopside, however, which showed no abrupt drop in the amount of bases leached away, and still developed the most intense acidity of any of the minerals. Olivine on the other hand showed a sudden falling off in the weight of bases extracted in each leaching and yet remained alkaline throughout the entire leaching period of forty two days. There was a noticeable change in the physical characteristics of the olivine, however, as the leaching progressed. A considerable quantity of material closely resembling beach sand, accumulated and it seems probable that upon leaching, SiO_2 is one of the products. The formation of SiO_2, however, cannot be the entire explanation for if such were the case the bases extracted would continue to be leached out in fairly constant amounts. This sudden fall in amount of material removed cannot be ascribed to the SiO_2 but may be due to a protective coating developing around the particles and inhibiting solution.

Tremolite shows an unusual solubility of bases in comparison with the other minerals. In forty two days it was soluble to the extent of 7% by weight and was still alkaline in reaction. A recently formed soil containing a large amount of tremolite would be able to maintain a neutral or alkaline reaction of the soil for many years.

Acidic Properties of Acid Residues Formed from Minerals.

After these minerals had been leached for forty two days the acidity of each as measured by the Truog test was determined. The hydrogen ion concentrations of suspensions of the minerals were also determined by means of the hydrogen electrode. The suspensions

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were made by shaking 5 grams of mineral with 25 cc. of water for four minutes. A Leeds and Northrup potentimeter accurate to within .05 of a P_H value was used in this determination.

Table 2.

The acidity of leached minerals as indicated by the Truog test, litmus paper and P_H determinations.

Minerals	Truog test	Litmus paper	P_H
Kôlin	Slight+	Acid	5.20
Muscovite	Medium	Acid	5.59
Olivine	Not acid	Neutral	6.60
Diopside	Slight	Acid	3.02
Tremolite	Not acid	Alkaline	8.03
Orthoclase	Very slight	Neutral	6.15
Biotite	Medium	Acid	5.82
Apophyllite	Slight	Acid	6.41
Natrolite	Very slight	Acid	6.68
Chrysocolla	Medium	Acid	5,48

That there is a difference in the character of the acids formed from the different silicates upon weathering is shown quite clearly by the determination of their P_H values. The hydrogen ion concentration of the suspension of the extracted diopside is equivalent to a 1/1000 N acid solution and results from a mineral which reacted basic to litmus before leaching and which has had only 2% of its weight dissolved and removed.

These differences in the acidity of residues from various minerals leads to the conclusion that the different molecular structures are an important consideration in the strength of acids which are formed on leaching. The structural differences of the minerals are quite marked according to the formulas developed by Clarke to explain the known properties of the various silicates. It seems quite probable that some of the minerals would tend to maintain their original structural relations even upon the replacement of bases and that the resulting compounds would be quite

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variable in their acidic properties.

Importance of Organic Matter in Soil Acidity.

The extent to which the organic matter contained in soils modifies their acidic properties was studied by comparing the acidity of four soils with the acidity of the mineral matter remaining upon removal of the organic matter from the soils. The organic matter was removed by two different methods.

The first method for removal of the organic matter was by means of oxidation with hydrogen peroxide. Forty gram samples of soil were placed in erlenmeyer flasks and 40 cc. of 3% hydrogen peroxide added. Checks were run using water in place of hydrogen peroxide. As the hydrogen peroxide became dissipated which was shown by the absence of bubbles on shaking, more was added. The oxidation was carried on at room temperature for two weeks and then completed by heating from 40° to 50° C on a steam sand bath for one week. The practically complete removal of organic matter was apparent by the change in color from black to greyish brown.

The eight samples were then thrown on a büchner filter, dried and the Truog test and P_H determinations made.

It was thought that there might have been some soluble sulphates, nitrates, chlorides, etc. formed during the oxidation of the organic matter which upon dissolving in water would enter into a reaction with the acid silicates and increase the acidity of the solution. In order to prevent this, any soluble salts present were removed by leaching 20 g. samples of soil with 300 cc. of water. The soil was dried in the air and the Truog test and P_H

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determinations were repeated.

Table 3

Acidity of acid soils before and after removing organic matter with H_2O_2

	Truog test		P_H determination	
	Before oxidation of organic matter	After oxidation of organic matter	Before oxidation of organic matter	After oxidation of organic matter
Plainfield Sand	Slight+	Slight+	5.41	4.99
Brown Silt Loam	Medium -	Medium+	6.26	4.79
Black Silt Loam	V.Slight	Slight+	7.39	4.89
Brown Silt Loam	Medium -	Strong -	6.37	4.50

Table 4

Acidity of the same soils reported in Table 3 after leaching with 300 cc. of H_2O

	Truog test		P_H determination	
	Before oxidation of organic matter	After oxidation of organic matter	Before oxidation of organic matter	After oxidation of organic matter
Plainfield Sand	Slight+	Slight +	6.72	5.72
Brown Silt Loam	Medium	Medium +	6.26	5.07
Black Silt Loam	V.Slight	Slight +	7.39	5.23
Brown Silt Loam	Medium -	Medium -	6.14	4.96

The mineral residues of the soil remaining upon removal of the organic matter with hydrogen peroxide give a stronger acid reaction than the original soils. From the results obtained from the weathering of minerals this would be expected. The hydrogen peroxide oxidizes the protective coating of waxy material which covers many of the soil particles and leaves a clean mineral surface. This increased amount of surface which has the opportunity of exerting

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its acidic properties probably greatly increases the acidity as measured by the Truog test and P_H determinations.

Another factor which causes an increased acidity is the absence of the buffer action of organic matter. That this is an important factor is shown by the P_H of the black silt loam soil as given in Table 4. The soil is very high in organic matter and alkaline in reaction but upon removal of the organic matter the remaining soil material is very acid in reaction.

The soil material after treatment with hydrogen peroxide showed a slight decrease in acidity upon washing with 300 cc. of water. This is probably due to the removal of small amounts of soluble salts and acids which were formed during the oxidation with hydrogen peroxide.

The second method used for the removal of organic matter was by means of heating the soils to constant weight at 200° C in an electric oven. The acidity was then determined as before. Several of the weathered minerals were similarly heated to 200° C and the effect of the heat upon their acidic properties noted by means of the Truog test.

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Table 5

Acidity of acid soils before and after removal of organic matter by heating.

	Truog test		P_H determination	
	Before oxidation of organic matter	After oxidation of organic matter	Before oxidation of organic matter	After oxidation of organic matter
Plainfield Sand	Medium +	V. Slight	5.53	6.43
Brown Silt Loam	Strong +	V. Slight	6.01	6.59
Black Silt Loam	Medium -	Not acid	6.31	7.34
Brown Silt Loam	Strong +	V. Slight	6.18	6.86

The removal of organic matter by means of heating to 200° C for several weeks reduced the acidity as measured by the Truog test to almost nothing. The effect of the heat upon the silicates is not a factor in the reduction of the acidity of soils. This was found to be true upon heating the acid minerals under similar conditions to those which the soil had been subjected. In every case the minerals which had been heated were more acid to the Truog test. This increase was not great, but noticeable. The decrease in the acidity of the soil is quite likely due to the drying of the remaining organic matter around the soil grains, thus preventing the solution of the mineral matter. This seems very probable since the appearance of the soil grains under the microscope did not reveal the clean surfaces which were noted when hydrogen peroxide was used to oxidize the organic matter.

From these results it may be concluded that organic matter contributes very little to the acidity of mineral soils. It is still probable, however, that the acidity of peats and other soils very high in organic matter may be due largely to organic acids.

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The relation of adsorption to soil acidity.

Upon the addition of a soluble salt to an acid soil in water there is an increase in the acidity of the solution and a decrease in the concentration of the basic constituent of the salt added. This has been explained by some investigators as due to adsorption by the soil of the base formed upon the hydrolysis of the salt in water. The adsorption of the base upon the surface of the soil particles would leave the other product of hydrolysis, the acid, in solution.

Since adsorption is a physical phenomena, a substance which is chemically inert and has a high adsorptive capacity is best suited for experiments on this subject. Charcoal is such a substance and accordingly was used in the following determinations. Three kinds of charcoal were used, - sugar, blood and animal charcoal. The blood and animal charcoal contained considerable material other than carbon for upon ashing, 17% of the blood charcoal and 48% of the animal charcoal was not volatile. The sugar charcoal was very pure and contained only 1.04% of ash which was reduced by leaching with carbonated water to .4% of non volatile material.

Since, as mentioned, it has been found that upon the addition of a salt to a soil in water there is an increase in soluble acidity, a similar procedure of adding a salt to charcoal in water, was followed, and the acidity of the solution noted. Normal and neutral solutions of two salts, $CaCl_2$ and $Ca(CH_3COO)_2$ were used. In every case 1 gram of charcoal was shaken with 25 cc of the normal salt solutions for five minutes and a reading of the suspension was then made electrometrically. Some trouble was encountered at first with the electrode becoming coated with charcoal but this was overcome by

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slowly bubbling hydrogen in at the bottom of the electrode container.

Table 6

Effect of different charcoals upon the hydrogen ion concentration of salt solutions.

	P_H of liquid in contact with charcoal.			P_H of original solutions
	Sugar Charcoal	Animal Charcoal	Blood Charcoal	
$CaCl_2$	7.18	3.59	7.08	7.20
$Ca(Ac)_2$	7.19	3.04	6.98	7.15
H_2O	7.06	4.48	7.95	7.07

The data presented in Table 6 are the average results of three determinations.

From the results given in Table 6 it appears that no acids are formed by adsorption upon the addition of a neutral salt to a substance of high adsorptive capacity. Due to the large amount of material contained in the animal charcoal which is not chemically inert, any change in acidity upon the addition of a neutral salt to this charcoal cannot be ascribed to adsorption. That the material remaining upon ashing the animal charcoal is active chemically is shown by the P_H of the water suspension. The results obtained with the blood charcoal are subject to the same criticism. This is not true, however, with the sugar charcoal which is very pure and in this case no acidity developed upon the addition of a neutral salt.

Since the amount of acidity caused by adsorption is beyond detection, the large amount of acids formed upon adding a neutral salt to an acid silicate are probably due to a chemical reaction between the acid silicate and the neutral salt to form a soluble acid.

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Discussion.

Upon weathering minerals with carbonated water a material is obtained which has acid properties similar to those exhibited by mineral soils. These acid properties are due to the presence of acid silicates which have been formed by removal of bases by the solvent action of carbonic acid. The acid silicates formed from different minerals have different acidic properties.

The rate at which minerals become acid upon weathering is quite variable, likewise the intensity of the acids formed so that the acidity of any soil will depend upon the kind of original minerals contained in the soil and the extent of their weathering. Since muscovite and orthoclase are found in considerable quantities in most of the soils of the United States and since these minerals become acid quite readily it is merely a matter of subjecting most soils to sufficient leaching in order to make them acid.

From the results obtained in this work the conclusion may be drawn that by far the most important factors to consider in the formation of acid soils are the acid silicates formed upon the weathering of the original mineral matter composing the soil.

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Summary

In order to study some of the acid properties of the acidic residues of minerals and their relation to acid soils, ten minerals ground to pass a 100 mesh sieve were weathered with five times their weight of carbonated water renewed daily for forty two days. The amount of material dissolved every two days was determined by filtering and evaporating the solutions and weighing the dissolved material. The point in the leaching where the minerals became acid was noted by placing litmus paper in contact with the minerals after each extraction and noting the reaction. The acidic properties of the residues were studied by determining the acidity with the Truog test and by means of the hydrogen electrode.

The importance of organic matter in affecting the acidity of mineral soils was also noted by removing the organic matter by two methods. Four soils quite high in organic matter were treated with 3% hydrogen peroxide and the concentration maintained by adding 4 cc. of 30% hydrogen peroxide at frequent intervals until the organic matter was almost entirely oxidized. The second method was to heat the samples of soil to 200° C in an electric oven until they came to constant weight. The acidity according to the Truog test and P_H values was determined upon each of the soils before and after the treatments outlined.

The amount of acidity which might be ascribed to adsorption was studied by adding 25 cc. of normal solutions of $CaCl_2$ and $Ca(Ac)_2$ to 1 g. samples of sugar, blood and animal charcoals and measuring the change in hydrogen ion concentration electrometrically.

The weathered minerals became acid in the order, kaolin,

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natrolite, pyroxene, muscovite, biotite, chrysocolla, orthoclase and apophyllite. The minerals olivine and tremolite remained alkaline throughout the entire leaching period. There was a large variation in the P_H values of the water suspensions of the acid silicates indicating the formation of acid silicates of different structure upon weathering and accordingly different acidic properties. The acidic material formed from diopside had a P_H of 3.02 which is equivalent to a 1/1000 N solution of acid.

Upon removal of organic matter with hydrogen peroxide the remaining material was more acid, while upon removal by heating to 200° C the acidity was reduced to almost nothing. This is thought to be due to an increased surface of acid silicates exposed upon treatment with hydrogen peroxide since it was observed to readily remove the waxy coating surrounding the soil grains. This coating upon heating, however, became dry and hard and the effective surface of the silicates was thus greatly reduced.

The change in acidity upon adding a neutral salt to sugar charcoal was not detectable electrometrically. With blood and animal charcoals the amount of acidity was slight upon addition of a salt and not nearly as great as that observed under similar conditions with an acid soil. The results obtained indicate that adsorption is of no importance in causing soil acidity.

The reason that some soils are much more acid than others seems to be due to the larger amount of certain minerals which they contain, which upon weathering leave comparatively strongly acidic residues. Muscovite, biotite, diopside and feldspar weather quite readily into strongly acidic residues and are found widely distributed in rocks and soils which, along with certain other minerals may account for the highly acidic character of some soils.

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References.

(1) Way, J.T. 1850 On the power of soils to absorb moisture. In Jour. Royal Agr. Soc. England, V. 11, p. 313-366.

(2) Lemberg, H. 1870 In Zeitsch Deutsch. Geol. Gesell. V.22, p. 335 and 803; V. 24, p.187.

(3) Sullivan, E.C. 1907 The interaction between minerals and water solutions. U.S. Geol. Survey, Bul. 312.

(4) Cornu, F. 1905 Versuhe uber die saure und alkalische reaktion von mineralien, inbesondere der silikate. In Tschermack Min. und Pet. Mitt. V.24, p.417; V.25, p.89.

(5) Clarke, F.W. 1900 The alkaline reaction of some natural silicates. U.S. Geol. Survey. Bul. 167, p-156-158.

(6) Steiger, G. 1900 The solubility in water of certain natural silicates. U.S. Geol. Survey. Bul. 167, p.159-160.

(7) Daikuhara, G. 1914 Uber saure Mineralboden. In Bul. Imp. Cent. Agr. Exp. Sta. Japan. V. 2, No. 1, p. 1-40.

(8) Van Hise, C.R. 1904 A treatise on metamorphism. U.S. Geol. Survey Monograph 47.

(9) Clark, F.W. 1914 The constitution of the natural silicates. U.S. Geol. Survey. Bul. 588,

(10) Loew, O. 1913 Studies on acid soils of Porto Rico. Porto Rico Agr. Exp. Sta. Bul. 13.

(11) Conner, S.D. 1916 Interchange of bases in artificial zeolites. In Jour. Ind. & Eng. Chem. V. 8, p. 35.

(12) Robinson, W.O. 1914 The inorganic composition of some important American soils. U.S.D.A. Bul. No. 122.

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A Thesis Submitted for the Degree of
Master of Science.

By.

Charles Danziger Samuels.

University of Wisconsin - 1922.

Approved.

C. Truog

Major Professor.

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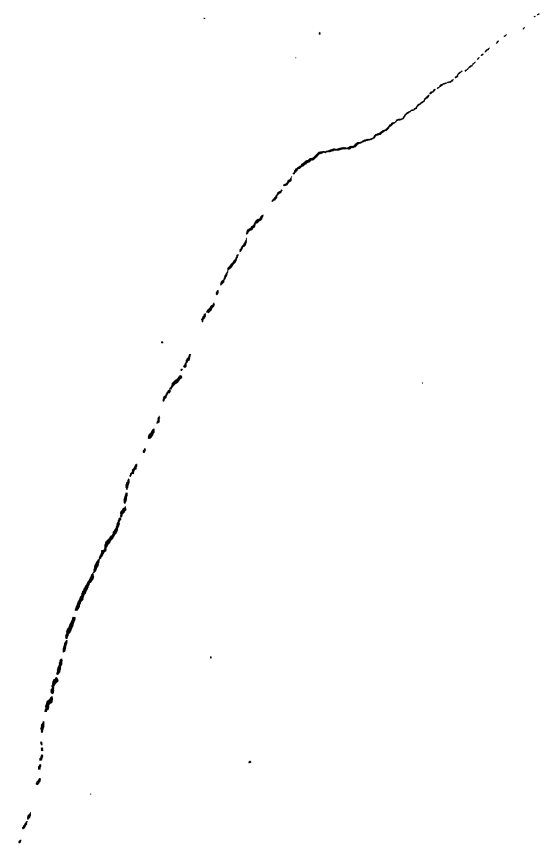

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